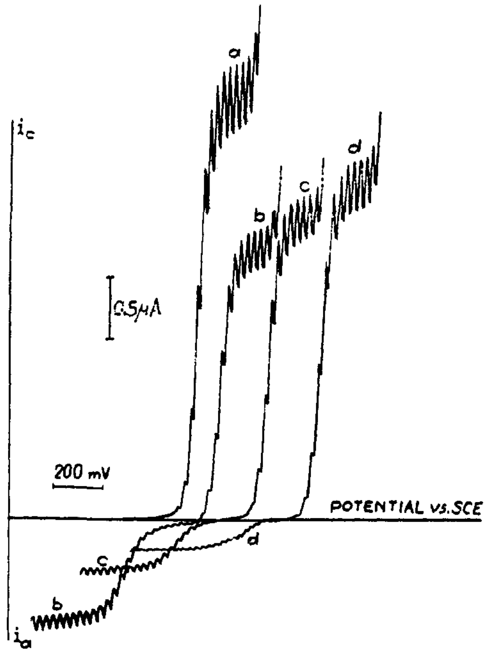

Figure 1. Polarographic curves of 1.3 × 10^{-3} M fluorenone in aqueous 38 vol % ethanol, 0.15 M NaOH, at 24°: (a) before electroreduction; (b) just after stopping a controlled-potential ($E = -1100 \pm 10$ mV *vs.* sce) electrolysis of 10-min duration; (c) 15 min later; (d) 30 min later. All curves begin at −0.3V.

It is difficult to explain why Michielli and Elving could not observe the anodic wave of benzpinacol.[1] Most probably, benzpinacol was absent in their sample at the moment of recording a polarogram. Perhaps their "commercial benzpinacol, used as received,"[1] did not already contain the compound, or the pinacol decomposed in solution prior to the measurement. Benzpinacol is easily oxidized to benzophenone, undergoes dismutation (1) in the presence of traces of base, and isomerizes to benzopinacoline. It must be thoroughly checked before use and the solutions must be prepared with necessary precautions.

Our conclusions are further supported by recent results of Nekrasov and Korsun[7,8] who studied the reduction of aromatic ketones on a rotating disk–ring electrode and found the anodic waves of benzpinacol and fluorenopinacol oxidation. All available evidence, with the exception of the report of Michielli and Elving, confirms that aromatic pinacols oxidize at a mercury anode.

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Oxidation of Benzpinacol in Alkaline Solution

Sir:

In a study of the electrochemical reduction of benzophenone in pyridine,[1] the statement was made that the oxidation of benzpinacol to benzophenone at the dme in alkaline aqueous ethanol solution (0.12 M NaOH in 68% (v/v) EtOH), as reported by Kemula, *et al.*,[2] could not be duplicated; this was ascribed to chemical decomposition of the pinacol before it could be measured. This work has been repeated under conditions which minimize decomposition of the pinacol and the oxidation previously reported[2] has been observed.

Three samples of benzpinacol—prepared chemically, electrochemically, and photochemically—were examined in the solution composition indicated by direct current polarography (scan rate of 0.2 V/min) and an anodic wave was observed with $E_{1/2}$ of −0.60 V (−0.58 V previously reported[2]), which decreases with time while the benzophenone cathodic wave increases. The rate of decrease in height of the anodic wave increases markedly as the alkalinity increases.

Acknowledgment. The authors thank James E. O'Reilly and Conrad O. Schmakel, who performed the experiments indicated.

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On Energy Localization of Approximate Molecular Orbitals[1]

Sir:

Energy-localized molecular orbitals (LMO's) obtained from the Edmiston–Ruedenberg (ER) method[2] are useful since they conform to intuitive ideas of chemical bonding. Applications of this method using semiempirical molecular orbitals are of particular interest since such MO's are at present readily available for a much wider range of molecules than are *ab initio* orbitals. Trindle and Sinanoğlu[3a] have recently applied the ER localization method to the CNDO/2[3b] molecular orbitals of several molecules; however, some of their results, especially for unsaturated systems, do not agree with the corresponding LMO's obtained from *ab initio* calculations.[4–6] In addition, it has been shown[7] that the fact that CNDO spherically averages electron-repulsion integrals can lead to an indeterminacy in the resulting LMO's. It is the purpose of this note to demonstrate that the less approximate INDO theory[8] is a more appropriate method to use for localization. Since INDO includes distinguishable one-center integrals, one would expect this method to give a more reasonable description of the atomic components of a molecule and thus of the canonical and localized orbitals as well.

[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2583.

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[3] (a) C. Trindle and O. Sinanoğlu, *J. Chem. Phys.*, 49, 65 (1968); (b) J. A. Pople and G. A. Segal, *ibid.*, 44, 3289 (1966).

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[7] M. D. Newton, submitted for publication.

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Table I.[a] Comparison of Edmiston–Ruedenberg, CNDO, INDO LMO's for Diatomics

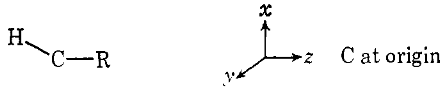
Molecule	Bond orbitals[b] INDO	Bond orbitals[b] ER[d]	Bond orbitals[b] CNDO	Lone pairs[c] INDO	Lone pairs[c] ER	Lone pairs[c] CNDO
Be_2	2 equiv (s)	None	1σ (s); 1π (s)	None	1σ (m)	None
C_2	2 equiv (s) 2 equiv (u)	4 ineq (u)	2 equiv π (s) 2 equiv σ (u)	None	None	None
N_2	3 equiv (s)	3 equiv (s)	3 ineq (s)	1σ (m)	1σ (m)	1σ (n)
F_2	1σ (s)	1σ (s)	1σ (s)	3 equiv (n)	3 equiv (n)	3 ineq (n)
BH	1σ	1σ	1σ	1σ on B (m)	1σ on B (m)	1σ on B (n)
HF	1σ pol to F	1σ pol to F	1σ pol to F	3 equiv on F (n)	3 equiv on F (n)	3 ineq on F (n)
LiF	3 equiv highly pol to F	3 equiv highly pol to F	1σ, 2 equiv π highly pol to F	1σ on F (n)	1σ on F (n)	1σ on F (n)
CO	3 equiv pol to O	3 equiv pol to O	1σ, 2 equiv π pol to O	1σ on C (n) 1σ on O (m)	1σ on C (n) 1σ on O (m)	1σ on C (n) 1σ on O (n)
BF	1σ pol to F	3 equiv pol to F	1σ, 2 equiv π pol to F	1σ on B (n) 3 equiv on F (l)	1σ on B (n) 1σ on F (m)	1σ on B (n) 1σ on F (n)

[a] equiv = equivalent; ineq = inequivalent. [b] s = symmetric; u = unsymmetric; pol = polarized. [c] n = negligible; m = moderate; l = large delocalization of lone pair onto other atom. [d] Edmiston–Ruedenberg: ref 4 of text.

Table II. INDO Localized CH and C–R Bond Orbitals in Polyatomic Molecules[a]

			A. CH Orbitals			
Atomic orbital	CH_4	C_2H_6	C_6H_6	C_2H_4	C_2H_2	H_2CO
$2S_C$	−0.3671	−0.3581	0.3834	−0.3996	−0.4892	−0.4366
$2P_{xC}$	−0.5661	−0.5582	−0.0059	−0.4760	0	−0.4552
$2P_{yC}$	0	0	0	0	0	0
$2P_{zC}$	0.2002	0.2193	0.5818	0.3282	0.5323	0.2884
$1S_H$	−0.7102	−0.7117	0.7108	−0.7050	−0.6869	−0.7183
θ(INDO)[b]	0	1.9		6.6		1.2
θ(*ab initio*)	0[c]	0.3[c]		2.0[d]		5.6[e]
			B. C–R Orbitals			
	C_2H_6	C_6H_6[f]	C_6H_6[g]	C_2H_4[g]	C_2H_2[h]	H_2CO[g]
$2S_C$	0.3713	−0.4200	−0.3106	0.3296	0.3242	0.2838
$2P_{xC}$	0	−0.0416	0.0212	0	−0.4561	0
$2P_{yC}$	0	0	0.4553	−0.5000	0.3420	−0.4481
$2P_{zC}$	0.6017	−0.5627	0.3880	0.3760	0.2481	0.3653
$2S_R$	0.3713	−0.4200	−0.3106	0.3296	0.3242	0.3223
$2P_{xR}$	0	−0.0416	0.0212	0	−0.4561	0
$2P_{yR}$	0	0	0.4553	−0.5000	0.3420	−0.5470
$2P_{zR}$	−0.6017	0.5627	−0.3880	−0.3760	−0.2482	−0.4265
ϕ(INDO)[i]			49.6	53	66.7	50.8 (C), 52.1 (O)
ϕ(*ab initio*)				56[d]	68[d]	60 (C)[e], 51.1 (O)

[a] R = O for formaldehyde, C for all other molecules. The Cartesian coordinates are with respect to the following axes (except benzene, see text)



[b] HCH bond angle minus angle between carbon hybrids of CH orbitals. [c] Reference 4. [d] Reference 5. [e] Reference 6. [f] σ bond. [g] Two equivalent banana bonds. [h] Three equivalent banana bonds. [i] Angle between C (or O) hybrid of banana bond and CC (or CO) axis.

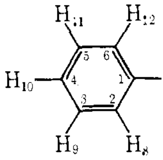
Table I compares the types of LMO's obtained from CNDO, INDO, and *ab initio*[4] canonical orbitals for a number of diatomic molecules. (In view of Newton's recent results,[7] some of the CNDO orbitals may not be unique.) The same bond lengths were used in all cases.[9] It is apparent that the general level of agreement with the *ab initio* calculations is superior for INDO. In particular, INDO reproduces the ER banana-like equivalent bond orbitals in molecules such as N_2, CO, and LiF and the equivalent lone pairs in HF and F_2. CNDO predicts one σ- and two π-type bond orbitals in CO and LiF, three inequivalent bond orbitals in N_2, and three inequivalent lone pair orbitals in HF and F_2. Both approximate methods incorrectly predict bonding orbitals in Be_2, while ER finds a somewhat back-bonded lone pair on each atom. For BF, ER finds three equivalent banana bonds polarized toward the fluorine while INDO yields three equivalent lone pairs strongly delocalized onto B. CNDO predicts one σ and two π bond orbitals. Localization of the *ab initio* canonical orbitals of C_2 yields four nonequivalent valence orbitals. INDO gives two equivalent LMO's symmetric in the two carbons and two equivalent but oppositely polarized orbitals.

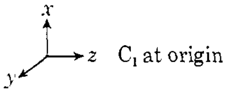
The INDO and CNDO localized orbitals for H_2O and NH_3 are both in fairly good agreement with the *ab initio* results.[4] The angle between the oxygen hybrids which contributes to the two OH bond orbitals in water is 90.2, 102.2, and 103.1° for ER, INDO, and CNDO, respectively. The corresponding values for the lone pair hybrids are 124, 115.2, and 115.2°. In all cases, the experimental bond angle of 104.5° was used. For ammonia, the angle between two nitrogen hybrids which

(9) B. J. Ransil, *Rev. Mod. Phys.*, 32, 245 (1960).

participate in the equivalent NH bond orbitals is 104.5, 105.3, and 105.0° from ER, INDO, and CNDO, respectively. The corresponding bond angle is 106.8°. All three calculations predict substantially less participation of the nitrogen 2s orbital in the lone pair of NH_3 than in N_2.

Table II lists the most important parts of the INDO CH and CR (R = C or O) bond orbitals for methane, ethane, ethylene, acetylene, benzene, and formaldehyde. It has been pointed out[4,10] that localization of the π orbitals of benzene leads to a continuous "infinity of sets of equally localized equivalent orbitals." [4] However, if the σ orbitals are included, this is no longer true and in fact INDO predicts three equivalent CC σ bonds and three pairs of equivalent banana bonds, *i.e.*, a Kekulé structure.





The similarity of the CH orbitals in methane and ethane is noteworthy. The slightly different s and p character in these two LMO's is in agreement with previous results[4] and is related to the fact that in ethane the CH orbitals no longer point along the bonds (Table II). The decrease in H participation from ethane to acetylene reflects the observed corresponding increase in C^-H^+ character. The carbon s character increases in the same direction.

INDO predicts that all of the unsaturated molecules have equivalent banana-like CR bonds in agreement with the *ab initio* calculations.[5,6] It is interesting to note that CNDO predicts σ and π orbitals for these molecules. The calculated angle between the carbon (oxygen) hybrid of the banana bond and the CR axis is in good agreement with the *ab initio* calculations except for formaldehyde. In the latter case, INDO (experimental geometry) also predicts the oxygen lone pairs to span an angle of 119.5° while Newton, using a slightly different geometry,[6,11] finds 132.4°. It should be pointed out that INDO yields a considerably better dipole moment (1.88) for this molecule than the *ab initio* calculation[11] (0.98). The experimental value is 2.34 D. In fact, one would expect the C hybrid to make a slightly smaller angle with the CO axis than the oxygen hybrid.[5] Ninety-one per cent of the electron density of the benzene banana bond is shared by the bonded carbons with the remainder primarily on the remaining carbons and symmetrically decreasing with increasing distance from the bond.

These results indicate that INDO is superior to CNDO for the study of localized orbitals. In later work, a more quantitative comparison of these INDO results with *ab initio* LMO's will be given. Future papers will also deal with application of the method to internal rotation as well as the transferability of and effect of chemical substitution on particular localized orbitals.

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Nuclear Magnetic Resonance Detection of Isomeric Structures of Bispyridoxylideneserinatoaluminum(III) and of Related Complexes in Deuterium Oxide

Sir:

Vitamin B_6 catalyzes many reactions of amino acids such as transamination, elimination of electronegative groups, and carbon–carbon bond fission. Many of these reactions also proceed at appreciable rates *in vitro* in the presence of pyridoxal and transition metal ions. Snell has proposed that amino acids form Schiff bases with pyridoxal which complex the metal ion as tridentate ligands, and he has suggested mechanisms by which these reactions may proceed.[1] The mechanisms in these metal-catalyzed model systems have been widely applied to pyridoxal enzyme catalyzed systems with considerable success, although many of the enzymes involved in pyridoxal catalysis do not require metal ions for activation.

Inasmuch as the aluminum(III) ion is one of the best metal ion catalysts for these model reactions, the structure of its complexes with pyridoxal–amino acid Schiff bases are of considerable significance. Recently Gansow and Holm[2] have published an nmr study from which they concluded that bispyridoxylidenealanatoaluminum(III) exists in two isomeric forms, the bis-tridentate octahedral complex (I) and the "dangling carboxyl" complex (II). In this paper are presented data indicating that the principle resonances of the nmr spectrum of bispyridoxylideneserinatoaluminum(III) are also consistent with the formation of three isomeric bis-tridentate octahedral complexes which are readily distinguishible because of a fortuitous juxtapositioning of the methyl group of one ligand and the magnetically anisotropic azomethine nitrogen of the other.

Pyridoxal and serine condense above pD[3] 7 to form pyridoxylideneserine (III) which can be detected by nmr.[6] As with the alanine–pyridoxal system,[2] Schiff base resonances can be detected at much lower pD's in the presence of aluminum(III) ion and these resonances are most logically assigned to the coordinated Schiff base. The resonances of the 4-CH, 5-CH_2, 6-H, and the amino acid portion of the Schiff base are within a few hertz of those for the coordinated Schiff base, but the 2-CH_3 resonances of the coordinated Schiff base are found as much as 100 Hz to higher field than those of the 2-CH_3 of the free Schiff base. This is shown in Fig-

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